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Shapes change of PbO nanoparticles produced by laser ablation in liquid

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Production of non-spherical crystalline nanoparticles by laser ablation in liquid has been demonstrated recently. Here we studied the shape variety of PbO nanoparticles prepared by laser ablation in deionized water and IPA. The key role of water in the formation of PbO non-spherical nanostructures was demonstrated. Only spherical nanoparticles have been obtained in isopropyl alcohol (IPA). PbO non-spherical nanostructures have been formed only in presence of water, which supports the growth mechanism by oxidation. Using mixture of IPA and water in various proportions and revealing the time and temperature dependences of non-spherical nanostructure morphology can be used for controlled growth of PbO non-spherical nanostructures.

1. Introduction

Laser ablation in liquid and especially in water gives an opportunity to produce metal and metal oxide “clean” colloids [1]. Avoiding additional chemicals for stabilization is of great importance for applications in medicine and life science. The control of the shapes of metal oxide non-spherical nanostructures can increase their application potential in nanodevices. PbO non-spherical nanostructures are used already in direct conversion X-ray detectors [2], photovoltaic devices [3], and electrocatalysis [4]. It elucidates recent interest to controllable production of PbO non-spherical nanostructures with desired shapes by various methods: ultrasonic liquid phase exfoliation of nanosheets from bulk PbO [4], electrodeposition in presence of oxygen resulted in formation of nanoplates [6, 7] and nanowires [6].

Recently, we have shown that the laser ablation of Pb target in water results in formation of the non-spherical nanostructures at target surface and in colloid [8]. The obtained formation of 3D nanostructures was attributed to growth of seed oxide nanoparticles and 2D plates by seedless growth. Unavoidable hot water treatment during laser ablation was proposed as an additional accelerating mechanism in the formation of non-spherical nanoparticles [8].

Here, we studied the shape variety of PbO nanoparticles prepared by laser ablation in water and isopropyl alcohol. The key role of the water in the formation of PbO non-spherical nanostructures was demonstrated.

2. Experimental

2.1. Laser ablation in liquid

The Pb target (99.9999% purity) with 50 mm diameter and 2 mm thickness was used for laser ablation in liquid. The target exposed at ambient conditions was rinsed in ultrasonic bath by turns with acetone,



isopropyl alcohol (IPA), and deionized water produced by Millipore Elix 10 (Merck, Germany) and finally purged by dry nitrogen. CCP oxygen plasma etching was used for homogeneous target surface preparations. Plasma etching was carried out for 30 min at 300 W power at the pressure 20 mTorr with 20 sccm oxygen flow (Plasmalab 80RIE, Oxford Instruments).

The Pb target was placed on the bottom of a dish and covered by 6.4 mm layer of deionized water (15 ml total volume) or 4.7 mm layer of 99.8% pure IPA (40 ml total volume). The glass Petri dish was used for IPA. The metal (anodized Al) dish used for water allowed realizing effective heat dissipation. The water temperature during laser ablation measured by IR thermal imaging camera H2640 (Nippon Avionics, Japan) was below 30°C.

Laser marking system Fmark-20 RL (LTC, Russia) equipped with pulse Ytterbium fibre laser (IPG Photonics, IRE-Polus, Russia) with 1062 nm wavelength, 100 ns pulse duration, and 21 kHz frequency was used for laser ablation. The focused laser beam (spot diameter 50 μm , fluence 51 J/cm²) scanned over the target area about 18 cm² with linear velocity 270 mm/s (30 lines/mm). The typical duration of the laser ablation process was about 4 min.

2.2. Nanoparticles imaging

The probe of the colloid (0.5 μl) was taken immediately after termination of the laser ablation process and dropped at Si plate. The duration of the drop drying process was about 3 min. The nanoparticles at the substrate were imaged by scanning electron microscope Merlin (Carl Zeiss, Germany).

3. Results and discussion

3.1. Laser ablation in water

The PbO non-spherical nanostructures (plates and rods) was obtained after the laser ablation in water along with spheroids (Fig. 1). The diameter of spheroids was from 10 to 100 nm. The shape of the plates changed between circle and hexagon, the thickness – from 10 to 20 nm, and the diameter – from 200 to 2000 nm. The width of the rods was from 60 to 180 nm and length – from 1 to 5 μm .

It is necessary to point out that some PbO plates were obtained in water after Pb target soaking in water at room temperature.

As it was shown by us earlier [7], the nanoparticles of different shapes also differ by phase: plates are β -PbO (orthorombic) and rods are α -PbO (tetragonal). PbO non-spherical nanostructures (rods and octahedra) were found only at target surface, but not in the colloid. This fact is attributed to sedimentation of the large particles. In this study, the various shapes of nanoparticles were obtained in water after time interval below five minutes after laser ablation termination including water exposure during drop drying. This fact allows evaluating the time interval necessary for formation of the PbO non-spherical nanostructures.

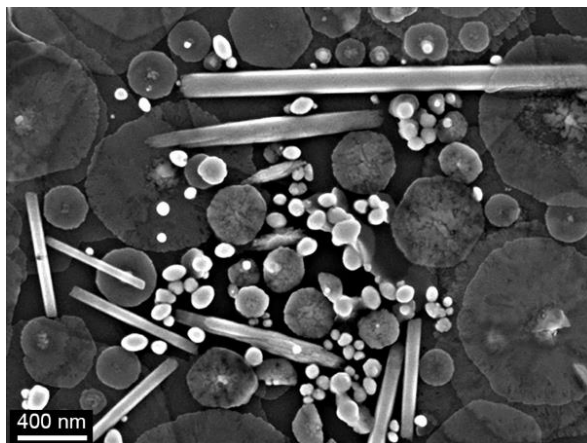


Figure 1. Plates, rods, and spheroids after laser ablation in water.

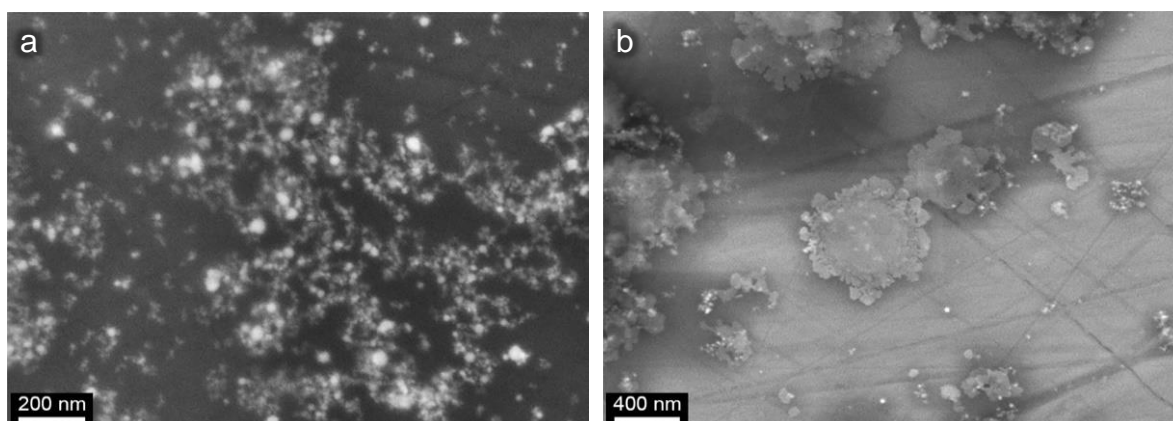


Figure 2. PbO nanoparticles: (a) produced by laser ablation in IPA, (b) after adding water.

3.2. Laser ablation in IPA

According to the supposed model, water is important for oxidation of Pb and growth of oxide nanoparticles. The control experiment – laser ablation in IPA – resulted in formation of the spherical nanoparticles only with diameter ranging from 10 to 50 nm (Fig. 2a). The Pb target soaking in IPA did not result in formation of any nanostructures both in liquid and at the target surface.

Addition of equal amount of deionized water in the IPA with spherical nanoparticles after laser ablation resulted in formation of PbO plates (Fig. 2b). The plates had irregular shapes and effective diameter from 500 nm up to few microns. These facts confirm the proposed mechanism of PbO plates seedless growth in water.

The observed results allowed using mixture of IPA and water in various proportions for controlling PbO non-spherical nanostructures growth. The time and temperature dependences of sizes and shapes of non-spherical nanostructures need further investigations.

4. Conclusion

The shape variety of PbO nanoparticles prepared by laser ablation in deionized water and in IPA has been studied. Only spherical nanoparticles have been obtained in IPA. PbO non-spherical nanostructures have been formed only in presence of water, which supports the growth mechanism by oxidation.

Mixing IPA and water in various proportions could be used for controlling PbO non-spherical nanostructures growth. The time and temperature dependences of sizes and shapes of non-spherical nanostructures need further investigations. The next step in this research is production of nanoparticles by laser ablation in water-IPA mixture.

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